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Prepared for the U.S. Department of Energy
Assistant Secretary for Environmental Management

Contractor for the U.S. Department of Energy
Office of River Protection under Contract DE-AC27-99RL14047

CH2MHILL
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P.O. Box 1500
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ELECTROCHEMICAL STUDIES OF CARBON STEEL CORROSION IN HANFORD DOUBLE-SHELL TANK WASTE

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ABSTRACT

This paper reports on the electrochemical scans for the supernatant of Hanford double-shell tank (DST) 241-SY-102 and the electrochemical scans for the bottom saltcake layer for Hanford DST 241-AZ-102. It further reports on the development of electrochemical test cells adapted to both sample volume and hot cell constraints.

Keywords: Hanford double-shell tanks, nuclear waste, carbon steel.

INTRODUCTION

The U.S. Department of Energy Site located at Hanford, Washington, contains six tank farms totaling 28 DSTs, each approximately 1 million gallons capacity. The DSTs currently

contain over 21 million gallons of highly alkaline high-level waste with approximately 80 million curies of radioactivity. The DSTs were designed to provide a 20- to 50-year service life and have been in service for 20 to 35 years. To meet the Hanford programmatic requirements, the DSTs will need to remain in service and exceed the original design life. To that end, chemistry control to mitigate corrosion processes becomes an important operating parameter. The chemistry limits pertaining to the supernatant and saltcake are presented in Table 1.[1]

TABLE 1
CURRENT HANFORD DST WASTE CHEMISTRY LIMITS

T<167 °F	
NO_3^- < 1M	NO_3^- > 3M
0.01M ≤ $[OH^-]$ < 8.0M	0.3M ≤ $[OH^-]$ < 10M
0.11M ≤ $[NO_2^-]$ ≤ 5.5M	$[OH^-] + [NO_2^-] \geq 1.2M$
$[NO_3^-] / ([OH^-] + [NO_2^-] < 2.5$	$[NO_3^-]$ < 5.5M

Electrochemical corrosion studies began as part of the DST integrity program. Supernatant samples are obtained in 250-mL containers. The saltcake tank samples arrive at the 222-S Laboratory hot cells in a core segment sampler. The core segment samplers will hold approximately 350 to 380 mL of tank waste. The saltcake waste is extruded vertically under argon into a 500-mL screw cap jar that also serves as the electrochemical cell, thus minimizing handling the waste more than is necessary.

Due to the high radiation of the sample, all electrochemical scans had to be carried out in a hot cell. The potentiostat was located outside of the hot cell with the leads introduced through inserts (dog legs to prevent radiation "shine"). To pursue the program, an electrochemical cell design was necessitated for both the smaller volume supernatant sample and the saltcake sample.

The cell design was proven against the ASTM G5-94[2] method.

EXPERIMENTAL PROCEDURE

Electrochemical Cell

Saltcake. The requirement to scan in various sections of the saltcake sample resulted in a screw cap lid with a radiation resistant polymer attached to the lid to allow the introduction of argon gas as well as impart stability for the reference electrode, working electrodes, counter electrode, and the thermocouple. Figure 1 shows the configuration of the lid.

Interrogation of the sample at various points is allowed by beginning the scans at the working electrode port. The second scan involved placing the reference electrode in the initial working electrode port and the working electrode in the original reference electrode port. For the third, fourth, and fifth scan, the lid is merely rotated approximately 45 degrees. This allows five scans at different areas of a heterogeneous sample.

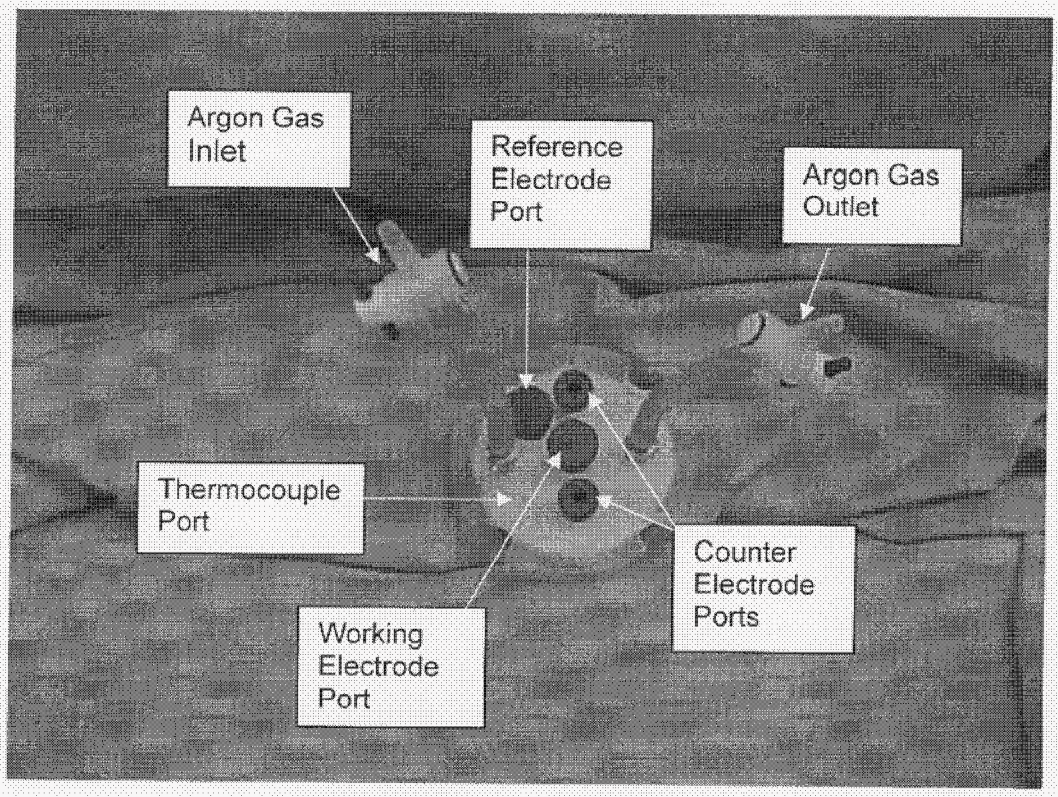

FIGURE 1 – Electrochemical Cell Lid

Supernatant. The supernatant used a 250-mL screw cap jar with the appropriate lid and a like geometric configuration for ports. However, the use of two counter electrodes in close geometry to the working electrode yielded aberrant current densities for the ASTM G5-94 method. The cell was tested using the working electrode and the counter electrode diametrically opposed and the reference electrode (saturated calomel) in the center port.

Scans. All scans were carried out using the appropriate metal coupon (supernatant A516, saltcake A537) ground to a 600-grit finish. The leads into the hot cell were tested first by chronoamperometry using a 48 kΩ resistor, then by the ASTM G5-94 method, both before and after the testing periods. The supernatant scans were carried out at the tank recorded temperature of 50 °C; the saltcake scans were carried out at ambient hot cell temperature of 25 °C (otherwise the saltcake would dry out).

RESULTS

Quality Control

The leads were checked using a 48 kΩ resistor and the ASTM G5-94 method. The potentiostat was used to run a chronoamperometry measurement against the resistor. The potential was set at 0.220 V against the 48 kΩ resistor (±10% tolerance). The potentiostat returned a current reading of 4.59E-06 A. This indicated the leads and instrument were functioning at a point source.

Figure 2 shows the results of the ASTM G5-94 method for the supernatant scans, and Figure 3 shows the ASTM G5-94 method results for the saltcake scans.

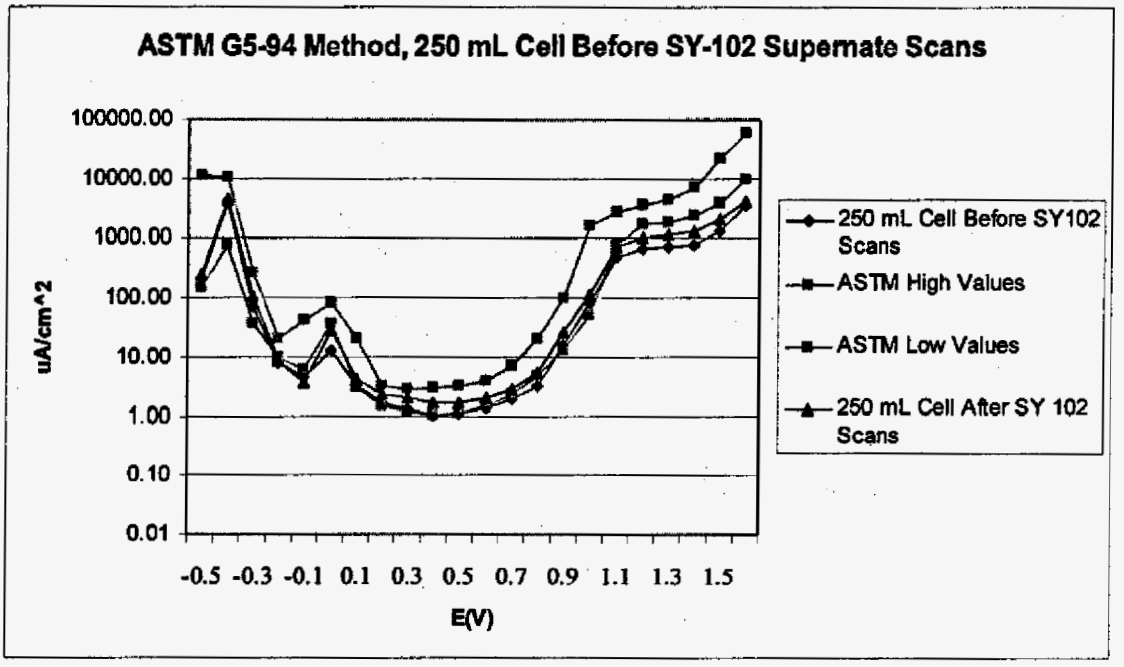

FIGURE 2 – The 250-mL Cell Response Before and After Supernatant Electrochemical Scans

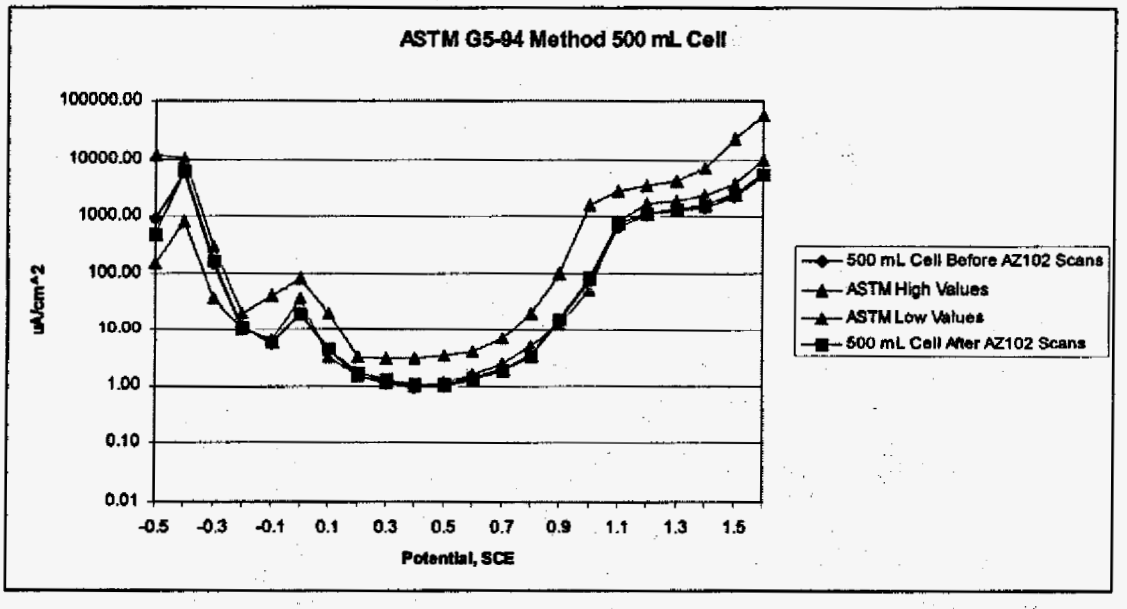

FIGURE 3 – The 500-mL Cell Response Before and After AZ-102 Saltcake Electrochemical Scans (before and after scans lay on top of one another)

Supernatant

The samples were subjected to cyclic scans that were carried out from -300 mV versus open circuit potential (OCP) to a current density of 2.5 mA/cm^2. Table 2 presents the

analytical data associated with the supernatant chemical analyses. Table 3 presents the data associated with and without argon purge. The argon purge and scan was performed after a cyclic potentiodynamic scan was performed on the as-received sample.

TABLE 2
ANALYTICAL RESULTS FOR TANK 241-SY-102 SUPERNATANT

Sample	OH^-, M	NO_2^-, M	NO_3^-, M	TOC,[a] µg/mL	pH
2SY-04-05	0.57	0.49	3.74	1.30E3	>13.5
2SY-04-06	0.58	0.50	3.79	1.27E3	>13.5
2SY-04-06 DUP	0.57	0.50	3.79	1.20E3	>13.5
2SY-04-07	0.55	0.49	3.71	1.29E3	>13.5
2SY-04-08	0.80	0.78	3.18	2.00E3	>13.5

[a] TOC = total organic carbon

TABLE 3
RESULTS OF ELECTROCHEMICAL CYCLIC POLARIZATION SCANS FOR TANK 241-SY-102 SUPERNATANT

Sample	Without Argon Purge			With Argon Purge		
	OCP,[a] (Breakdown potential) mV	Corrosion Rate (mpy)[b]	χ^{2c}	OCP,[a] (Breakdown potential) mV	Corrosion Rate (mpy)	χ^{2c}
2SY-04-05	-350 (450)	0.039	49.3	-540 (500)	0.014	83.7
2SY-04-06	-430 (480)	0.039	20.3	-360 (490)	0.018	47.9
2SY-04-06 DUP	-428 (450)	0.028	44.3	-580 (450)	0.012	44.1
2SY-04-07	-430 (450)	0.038	23.5	-560 (460)	0.013	59.1
2SY-04-08	-390 (460)	0.039	16.8	-583 (450)	0.019	31.4

[a] OCP = open circuit potential
[b] mpy = mils per year
[c] χ^2 = goodness of fit statistic, to the Stern-Geary equation, typical values for reasonably good fits will range between 2 and 100.

It should be noted that during the argon purge, there was vigorous foaming at low purge volumes, probably due to the high organic values as indicated by the TOC values in Table 3. To ensure the sample did not "boil over," argon was introduced very slowly and carefully watched until a "steady state" was obtained with the foaming response.

As seen in Table 3, corrosion rates ranged from 0.028 to 0.039 for non-argon sparged and 0.012 to 0.019 for argon sparged. The purging of the sample using argon did affect the OCP as indicated, perhaps by displacing oxygen from the sample. A typical scan for the supernatant is presented in Figure 4. As the scan indicates, there is no pitting propensity.

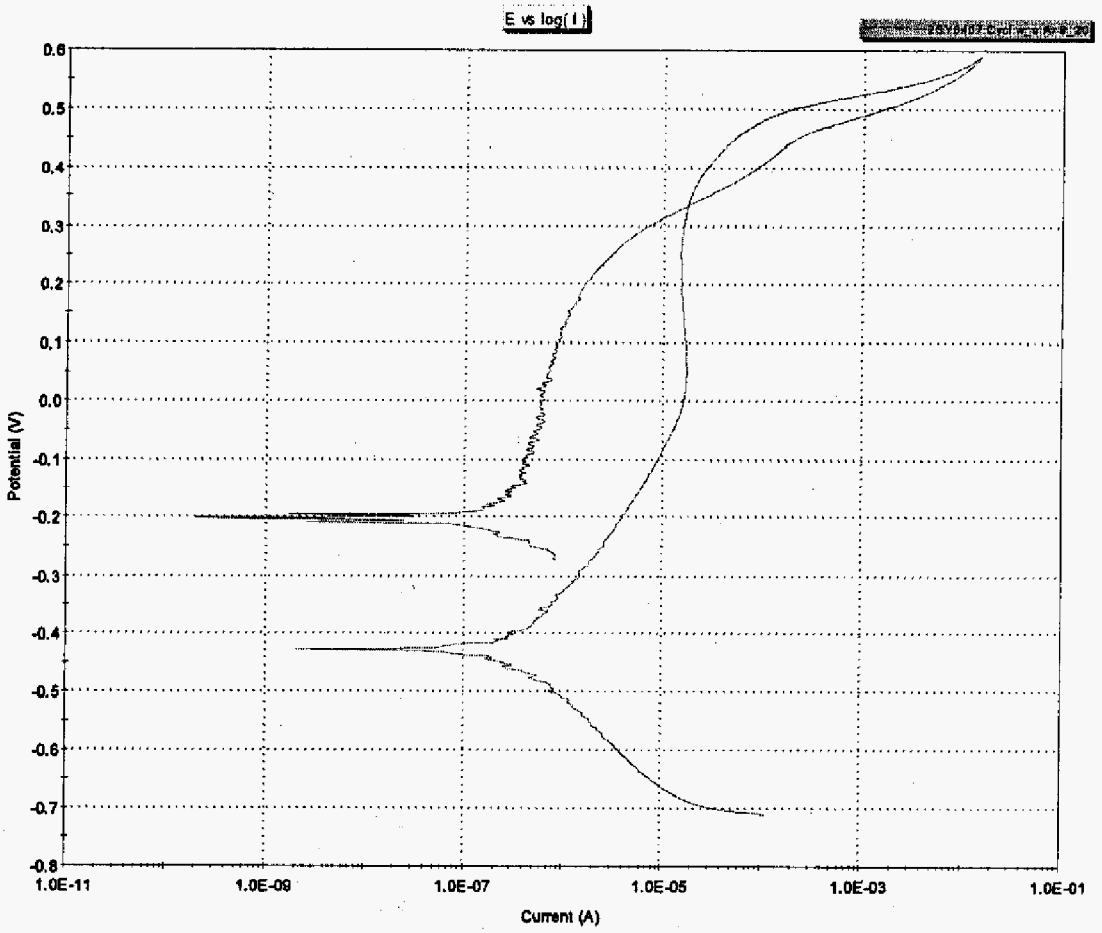

FIGURE 4 – Cyclic Potentiodynamic Scan (versus Saturated Calomel Electrode) for Tank 241-SY-102 Supernatant

Saltcake

Samples were obtained from the knuckle region of tank 241-AZ-102. The initial two core segment samples had to be combined for the initial testing, and a third core segment was taken for comparison at a later date. The first two samples (combined) were 19/19R1; the second retake sample was 19R3. Table 4 presents the chemistry associated with the saltcake.

TABLE 4
SLUDGE INTERSTITIAL LIQUID CHEMICAL ANALYSIS, TANK 241-AZ-102

Segment	% Water	pH	Calculated OH^- (M)	NO_2^- (M)	NO_3^- (M)
19/19R1	32	11.97	0.009	0.94	0.04
19R3	53	11.48	0.003	0.98	0.04

The sample 19/19R1 did show pitting propensity from the cyclic polarization potential scans at each point of the sludge interrogated. The reverse scans all returned at a higher current density. Table 5 presents the data obtained from the four sample sections of 19/19R1. Figure 5 shows a typical scan obtained from this sample.

TABLE 5
RESULTS OF ELECTROCHEMICAL CYCLIC POLARIZATION SCANS FOR TANK 241-AZ-102 SALTCAKE, SEGMENT 19/19R1

Sample Identification	OCP (mV)	General Corrosion Rate (mpy)	Breakdown Potential (mV)	χ^2	Maximum Current Density (mA/cm^2)
S04T000397	-232	0.0013	543	1.61	8.1
S04T000398	-208	0.0016	472	18.69	7.5
S04T000400	-243	0.012	550	8.87	6.8
S04T000401	-235	0.008	500	32.5	7.9

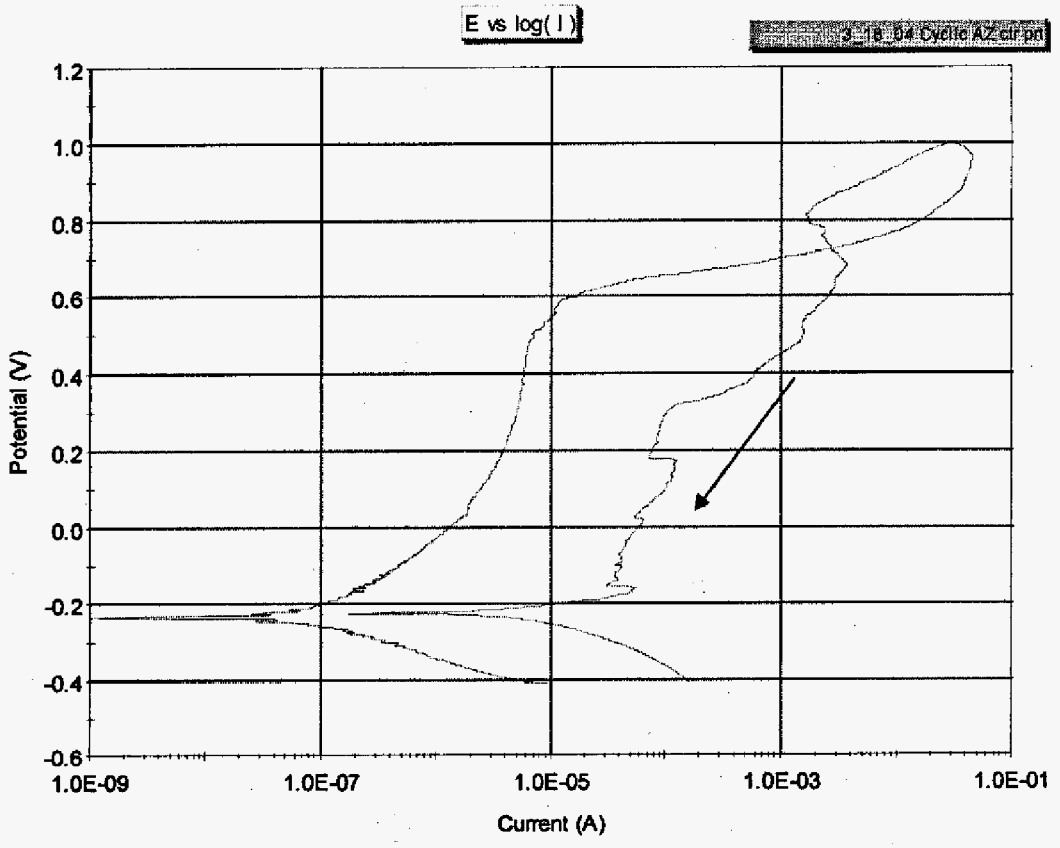

FIGURE 5 – Typical Cyclic Polarization Potential Scan Obtained with Segment 19/19R1, the Reverse Scan is at Higher Current Densities (arrow down)

For the sample 19R3, the cyclic scans did not indicate pitting propensity. Figure 6 shows a typical scan obtained from sample 19R3.

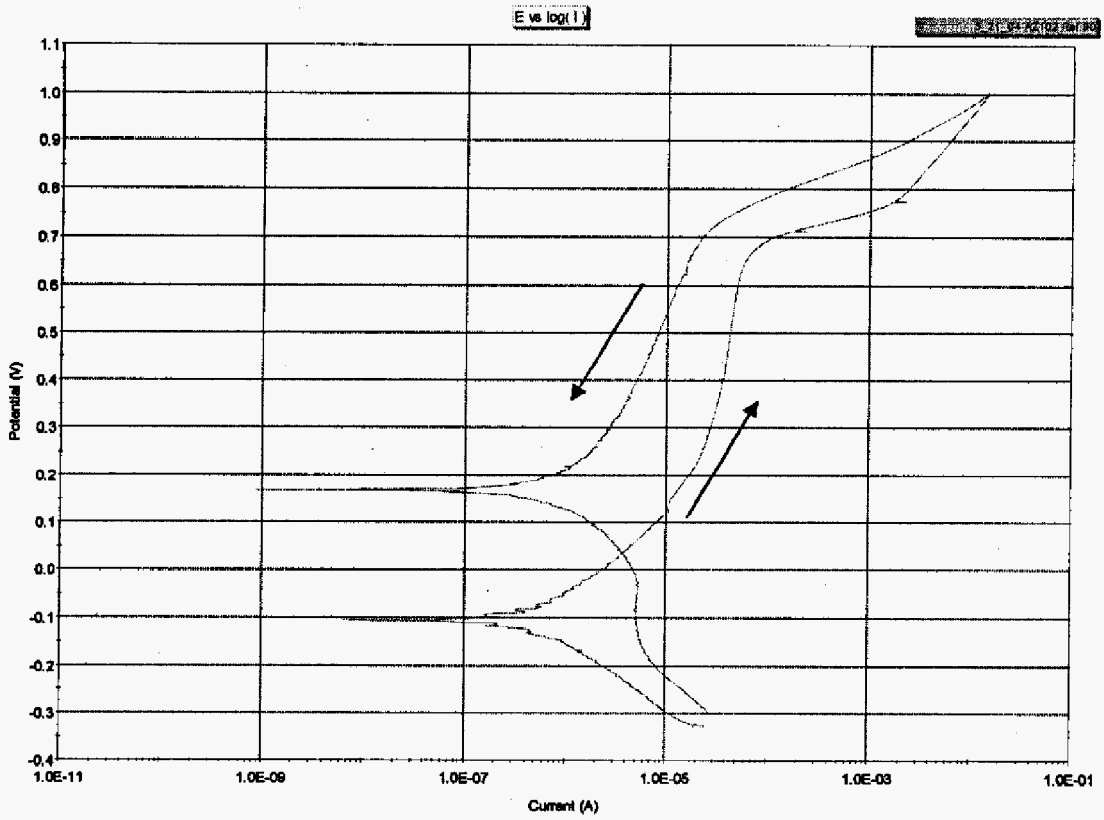

FIGURE 6 – Typical Cyclic Polarization Potential Scan Obtained with Segment 19R3, the Reverse Scan is at Lower Current Densities (arrow down).

During the course of sample 19R3, it was decided to use a tissue grinder and homogenize the sample under argon. The polarization curve was as shown in Figure 6. Table 6 presents the scan data from two scans of the as-received sample and the one homogenized sample scan.

TABLE 6
RESULTS OF ELECTROCHEMICAL CYCLIC POLARIZATION SCANS FOR TANK 241-AZ-102 SALTCAKE, SEGMENT 19R3

Coupon Identification	OCP (mV)	General Corrosion Rate (mpy)	Breakdown Potential (mV)	χ^2	Maximum Current Density (Ma/cm^2)
Ref Port 90 (before homogenization)	-106	0.056	714	31.94	2.5
Ref Port 180(before homogenization)	-153	0.02	634	36.47	2.4
After homogenization	-195	0.015	602	14.61	2.5

Due to the pitting propensity of the 19/10R1 sample, a coupon was placed in the saltcake and left at OCP for 8 weeks. Figure 7 is a scanning electron microscopy image of the test coupon after the 2-month OPC.

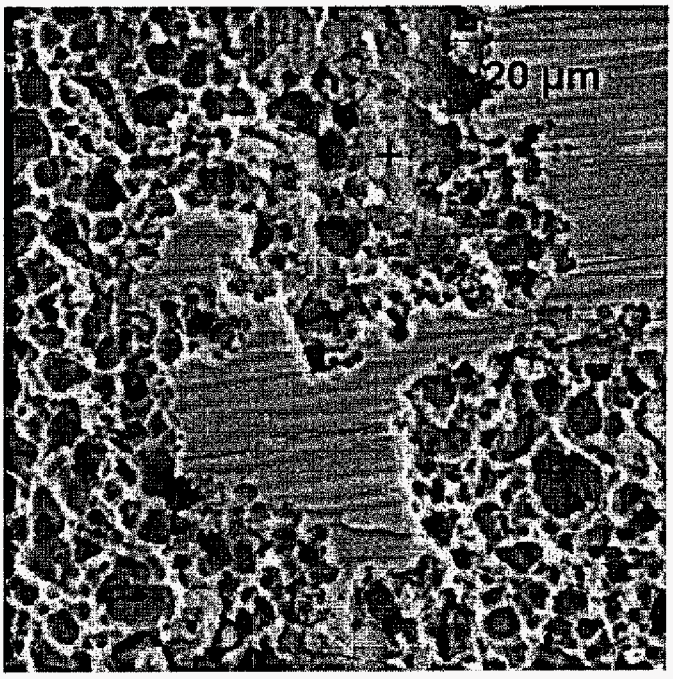

Figure 7 – Scanning Electron Microscopy Image of A537 Coupon Left in Sample 19/19R1 for 2 Months at Open Circuit Potential

Tables 7 and 8 compare the Hanford DST chemistry control parameters (Table 1) to the analytical chemistry of the supernatant and saltcake samples respectively. The out-of-specification parameter is noted by the bolded numbers.

TABLE 7
TANK 241-SY-102 SUPERNATANT CHEMISTRY COMPARED TO HANFORD DST CHEMISTRY CONTROL PARAMETERS.

	$[NO_3^-]$> 3M, T<167 °F		
	0.3M ≤ $[OH^-]$ < 10M	$[OH^-] + [NO_2^-] \geq$ 1.2M	$[NO_3^-] \leq$ 5.5M
2SY-04-05	0.57	**1.06**	3.74
2SY-04-06	0.58	**1.08**	3.79
2SY-04-06 DUP	0.57	**1.07**	3.79
2SY-04-07	0.55	**1.04**	3.71
2SY-04-08	0.80	1.58	3.18

TABLE 8
SAMPLE 19/R1 AND 19R3 CHEMISTRY COMPARED TO HANFORD DOUBLE-SHELL TANK CHEMISTRY CONTROL PARAMETERS.

	$[NO_3^-]$< 1M, T<167 °F		
	0.01M ≤ $[OH^-]$ < 8.0M	0.11M ≤ $[NO_2^-] \leq$ 5.5M	$[NO_3^-] / ([OH^-] + [NO_2^-]$ < 2.5
19/19R1	**0.009**	0.94	0.04
19R3	**0.003**	0.98	0.04

CONCLUSIONS

As indicated in Tables 7 and 8, some chemistry control parameters are not with the specified value set. However, the supernatant sample did not show pitting propensity but exhibited passive tendencies coming out of the anodic Tafel branch. This passivation may well be attributed to the high degree of organics present in the sample. Also, corrosion rates ranged from 0.028 to 0.039 for non-argon sparged and 0.012 to 0.019 for argon sparged. It is possible that the displacement of gases by the inert argon gas may be responsible for the smaller corrosion rate. The higher organic loading and the liquid sample allowing mass transfer processes to take place may well have played a role in the observed nonpitting propensity.

For the saltcake, however, in the *Compilation of Hanford Corrosion Studies* (ARH 1975),[3] it is stated that pitting attacks are more severe with carbon steel that is exposed to the simulated moist solid waste than to the simulated liquid waste. The pitting exhibited by coupons immersed in the tank 241-AZ-102 Core 313 Segment 19/19R1 sludge composite seemed to exhibit localized aggressive pitting. Segment 19/19R1 sludge composite, being drier, would contain more solids. In those places where the solids were against the coupon surface, interstitial liquid may become mass transfer limited and not able to passivate the metal surface. Segment 19R3 sludge was wetter and more liquid in physical form, which could cause the coupon surface to be "refreshed," much the same as a coupon tested in a liquid environment. That is, the interstitial liquid present in Segment 19R3 could reach the coupon surface and passivate reactive surfaces during the pitting process.

The anodic reaction of magnetite, which is composed of $Fe^{+2}(Fe^{+3})_2O_4$, is presented as follows:

$$Fe^{+2} + 2H_2O \rightarrow Fe(OH)_2 + 2H^+ \qquad (1)$$

K_{sp} of $Fe(OH)_2$ = 4.87E-17.

This reaction would result in an effective local pH of 8.5; the lowered pH and two free hydrogen ions available for bonding with aggressive ionic species, such as sulfates, fluorides, and chlorides, could generate conditions conducive to pitting. Additionally, for drier sludge, the reactions described above could take place under a solids deposit where the interstitial liquid cannot reach (mass transfer inhibited) and the carbon steel surface will not passivate but will continue to corrode.

Therefore, the percent moisture in the sludge in conjunction with hydroxide, nitrate, and nitrite concentrations may well play a role in mitigating the pitting processes.

ACKNOWLEDGMENTS

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